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13. ABSTRACT (Maximum 200 words) This project consists of a collaborative synthetic, processing, physical characterization, and theoretical program aimed at the rational design, construction, evaluation, and fundamental understanding of new types of maximum-performance molecule/polymer-based materials exhibiting high second-order ($\chi^{(2)}$) optical nonlinearities. Areas of emphasis include poled chromophore-functionalized glassy polymers, poled chromophore-embedded crosslinkable matrices, chromophoric self-assembled superlattices, the theoretical design and analysis of novel chromophores and chromophore environments, theoretical studies of poling dynamics, studies of optical damage phenomena, and fabrication of new types of NLO waveguides. Each research component of this highly interactive effort builds upon work already in progress as well as upon strong on-going collaborations in laser optics and quantum theory.					
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Final Technical Progress Report

AASERT94 Processing and Characterization Knowledge Base for Device-Compatible Second-Order Nonlinear Optical Polymers

F49620-94-1-0354

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Objectives

To delineate and understand those macromolecular architectural and processing features which maximize and stabilize second-order nonlinear optical polymer response and yield device-applicable materials. To develop instrumentation to characterize them.

Status of Effort

The two students involved in this AASERT program, Mark Davey (NU chemistry graduate student) and Paul Lundquist (NU physics graduate student) were involved in a joint NLO polymer research effort between Northwestern and IBM Almaden Laboratory. Davey worked with the group of Dr. R.D. Miller with the principal focus being to combine NU and IBM chromophore and polymer synthetic, processing, and characterization expertises. The work involved activities in both laboratories and has included chromophore synthesis, polymer synthesis, polymer processing (film fabrication, poling, curing), and NLO measurements. Polyimides with high $\chi^{(2)}$ responses and very high SHG temporal stability have resulted. One communication has already been published and several additional manuscripts are in preparation. Lundquist focussed on three, instrumentation-related topics. In the first, he used an optical parametric amplifier he constructed to explore $\chi^{(2)}$ dispersion in several classes of poled polymers identifying, in one instance, evidence for charge injection and charged chromophore aggregate formation. In a second activity, he developed a highly accurate and convenient transmission electrooptic characterization technique for thin organic films. Finally, Lundquist participated in the development of a unique hybrid waveguide device for electrooptic modulators and frequency doubling.

RESEARCH ACCOMPLISHED IN THE PAST CONTRACT PERIOD

I. Poled Polymers. Synthesis, Processing, NLO Characterization

The central goal of this research effort is to build the knowledge base needed to bring second-order polymeric NLO materials¹ all the way to useful photonic device technologies. To do so, we have closely coupled in-house activities with complementary efforts at IBM, ROITech, and Caltech. Our overall approach is *modular*, to allow efficient interchange/updating of chromophore and/or matrix building blocks with each advance in the state-of-the-art. We make extensive use of our in-house in situ poling/curing/real-time NLO response instrumentation to optimize poling/curing conditions. To neglect such optimization details, in our opinion, incurs the risk of missing important processing information. A separate section below outlines new techniques and facilities which will enhance our NLO polymer effort and that have recently come online.

A. Chromophore-Functionalized, Crosslinked Polyhydroxystyrenes.

Poly(*p*-hydroxystyrene) (PHS) is a commercially available (including electronic grade), robust ($T_d = 400^\circ\text{C}$), glassy ($T_g = 155^\circ\text{C}$) polymer that adheres tenaciously to various substrates and has been used as a deep-uv photoresist. It can be readily functionalized with a variety of hydroxyl-substituted chromophores and subsequently poled and crosslinked to yield glassy, high- T_g , high- $\chi^{(2)}/r$ thin films. A joint Marks-Ratner student, Millicent Firestone, carried out an extensive experimental/theoretical study of the NLO temporal characteristics of these materials as a function of macromolecular architecture, chromophore chirality, and processing conditions.² The key conclusions, which should be general to a great many classes of poled glassy polymers are:

1. $\chi^{(2)}(t)/r(t)$ doesn't always track T_g .
2. Polyfunctional crosslinking agents are far more effective in immobilizing the matrix than difunctional agents.
3. How the crosslinking is carried out (curing schedule) is crucial to optimum stability of chromophore alignment.
4. Stretched exponential and biexponential response decay behaviors are *statistically indistinguishable*. There are good theoretical reasons for this.
5. The KWW parameters for our materials classify them as Angell "intermediate glasses", and are *grossly different* from those of chromophore-doped guest-host materials.
6. The KWW/VTF parameters for these PHS-based materials are *grossly different* from those of chromophore-functionalized polyacrylates.
7. It is possible to model $\chi^{(2)}$ decay subsequent to poling using various modifications of the Smoluchowsky formalism. Important conclusions about rotational diffusion and macromolecular dynamics can be reached by studying r_{33}/r_{31} as a function of time. We conclude that such systems are *intrinsically heterogeneous* and that *glassy and rubbery regions coexist*.

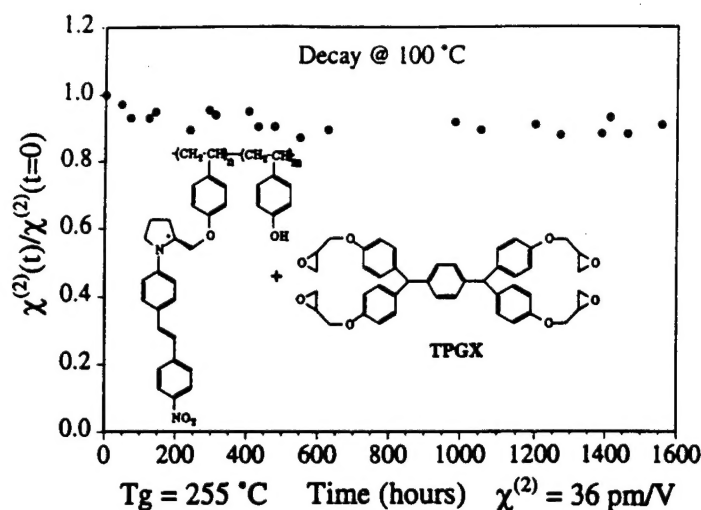


Figure 1. $\chi^{(2)}$ temporal characteristics in air of a poled, crosslinked, chromophore-functionalized poly(*p*-hydroxystyrene) film.

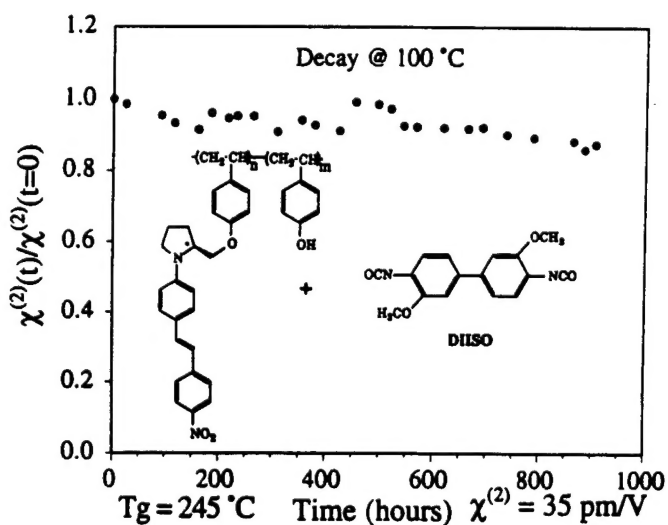
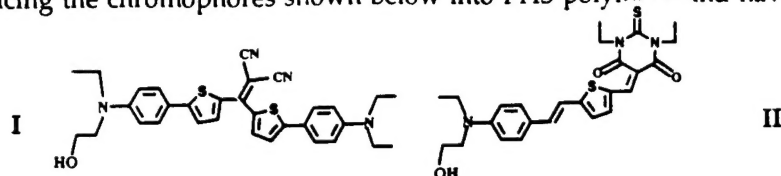


Figure 2. $\chi^{(2)}$ temporal characteristics in air of a poled, crosslinked, chromophore-functionalized poly(*p*-hydroxystyrene) film.

These observations led Eric Crumpler (a top-notch African-American graduate student, now postdocing at M.I.T.) to introduce higher β chromophores and polyfunctional crosslinking agents.³ The results are high- T_g (up to 255°C) thin films with excellent NLO response ($\chi_{33}^{(2)} \approx 36$ pm/V at 1064 nm; $r_{33} \approx 10$ pm/V at 1300 nm) and temporal stability at 100°C in air (Figures 1, 2). Studies of aging at 100°C as a function of various atmospheres showed that the temporal stability of the response was *adversely affected by* O_2 but not by H_2O vapor.⁴ Eric also fabricated rib waveguides by RIE.

Poly(*p*-hydroxystyrene) is an excellent platform with which to build new families of class B $\chi^{(2)}$

polymers. Working with Drs. Alex Jen (ROITech) and R. Seth Marder (Caltech), we are now introducing the chromophores shown below into PHS polymers and have been using our real-time



in situ poling/curing/ $\chi^{(2)}$ instrumentation to optimize poling and crosslinking of these materials. The results to date include very large responses.⁵ We are currently working with Drs. Jen and Marder to improve the thermal stability of these materials. ROITech is also planning to send a researcher to our laboratory to collaborate with us on optimizing the poling protocol for the ROITech poled polymers. A confidentiality agreement is in place between ROITech and Northwestern.

B. Poled Polyimides/Polyureas

Using simple Michael addition and urea condensation methodologies, we have produced

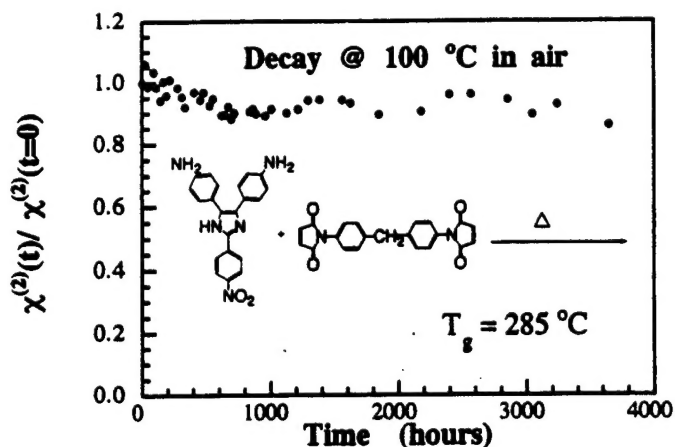


Figure 3. $\chi^{(2)}$ temporal stability of a poled, crosslinked chromophoric polyimide.

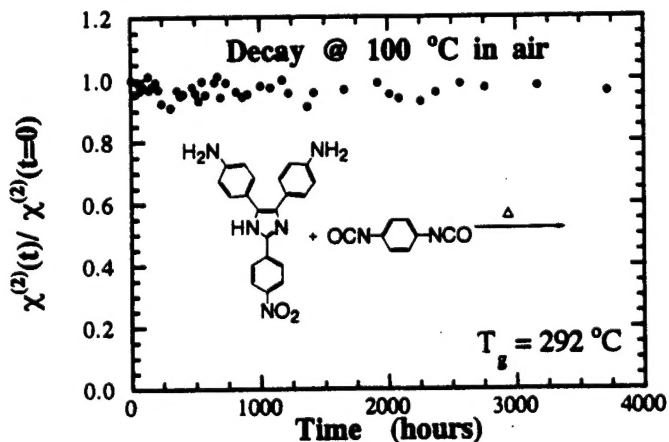


Figure 4. $\chi^{(2)}$ temporal stability of a poled, crosslinked chromophoric polyurea.

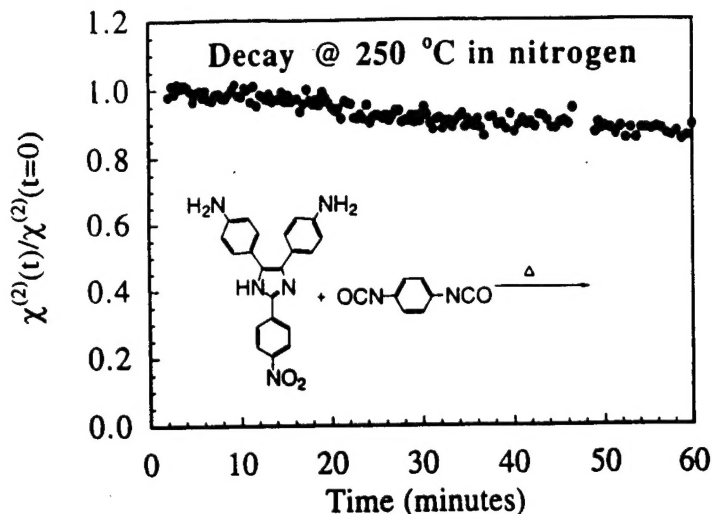


Figure 5. High temperature $\chi^{(2)}$ temporal stability of a poled, crosslinked chromophoric polyimide.

several classes of ultra-high-T_g materials with excellent NLO temporal stability at 100°C and 250°C (Figures 3-5).⁶ Typical NLO parameters after initial decay (of which there is very little) are $\chi_{33}^{(2)} = 35\text{-}50$ pm/V at 1064 nm; $r_{33} = 5\text{-}7$ pm/V at 1300 nm). Importantly, both of these model systems utilize readily synthesized or commercially available building blocks. Because of the modularity of the synthetic approach, we are now ready to "plug in" high- β -chromophore modules (see following section) that one of the Northwestern NLO chemistry graduate students has developed during an internship with Dr. Robert Miller's group at IBM Almaden. A formal joint study agreement is in place between IBM and Northwestern on this project.

Our interest in the $\chi^{(2)}$ decay dynamics of poled chromophoric polyimides and polyureas prompted us to study temporal characteristics as function of aging atmosphere (Figure 6).⁷ As shown below, *atmospheric/environmental effects on $\chi^{(2)}$ temporal stability are dramatic, and quite different from the poly(hydroxystyrene) results mentioned above.* Clearly we need to understand these degradative effects better if device stability is to be optimized.

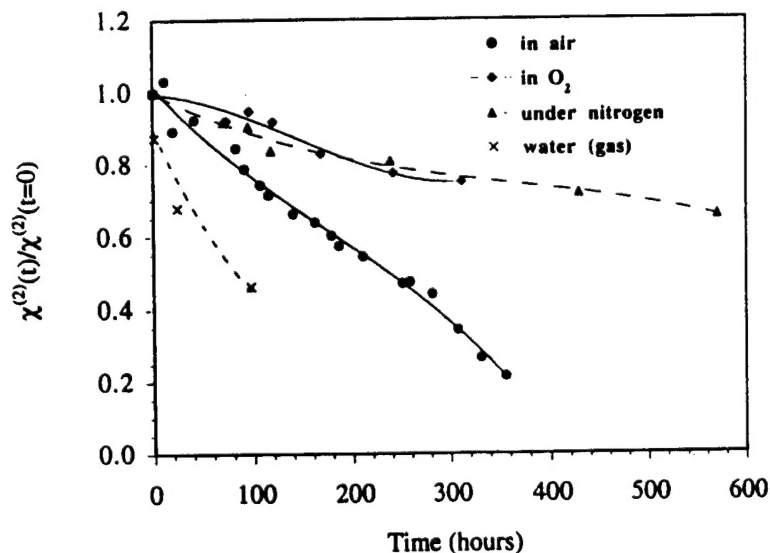


Figure 6. Environmental effects on the $\chi^{(2)}$ stability of a poled, crosslinked chromophoric polyurea at 200°C.

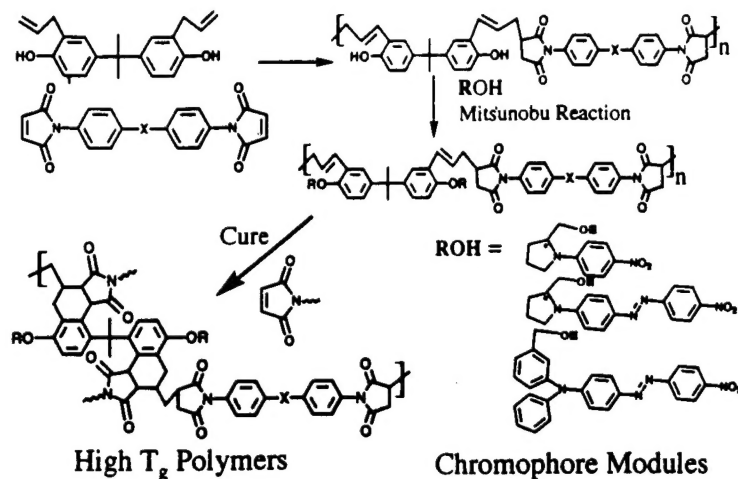


Figure 7. Modular approach to high- T_g chromophore polyimides.

Another modular approach to poled polyimides employs bis(maleimide)/ene reaction chemistry which was originally developed by Ciba-Geigy and NASA⁷ for ultra-high-temperature/-stability aerospace resins. Using commercially available reagents, a prepolymer is synthesized which can then be readily hybridized with a variety of hydroxyl-functionalized chromophore modules (Figure 7).⁸ Although we are still optimizing poling and curing, preliminary results are very encouraging ($T_g = 320^\circ\text{C}$; $\chi_{33}^{(2)} \sim 35 \text{ pm/V}$ at 1064 nm; $r_{33} \sim 8 \text{ pm/V}$ at 1300 nm; see below). Importantly, these matrices are ideal for incorporating the latest generation ROITech and

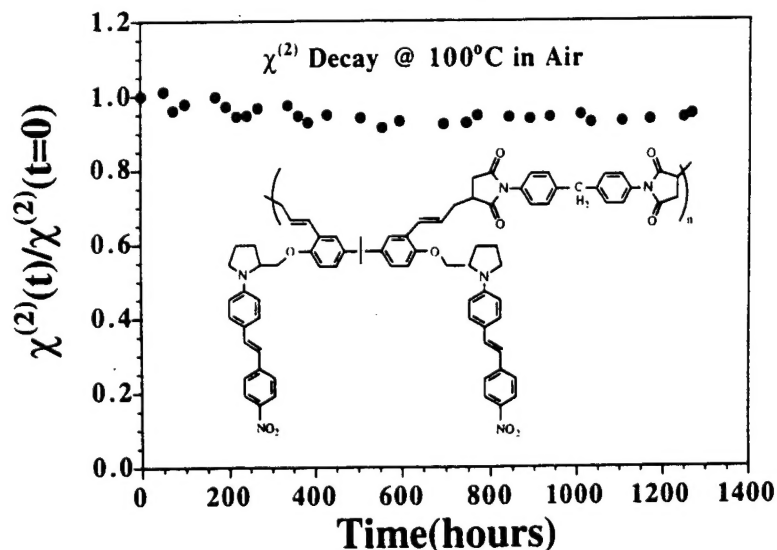


Figure 8. $\chi^{(2)}$ temporal stability of a poled, crosslinked chromophoric polyimide.

Caltech chromophore modules. This will be undertaken in the coming contract period.

C. Consequences of Charge Injection and Polymer Aging in Oxidative Environments.

Little is known or agreed upon regarding degradative processes that second-order NLO polymers may undergo during poling and high-temperature service. Consequences may include

undesirable optical losses at long wavelength.⁹ To better understand these factors, we began with a model system (DANS/PMMA) in which there was literature evidence¹⁰ for charge injection by in-plane poling electrodes. What was detected in our study¹¹ was the development of *very significant absorption in the $\lambda > 650$ nm region which could be correlated with charge injection*. More importantly, the long wavelength features (Figure 9) were shown to be NLO-active using in house optical parametric amplifier (OPA) instrumentation (see below). Here the $\chi^{(2)}$ (dotted lines) response at 600 nm derives

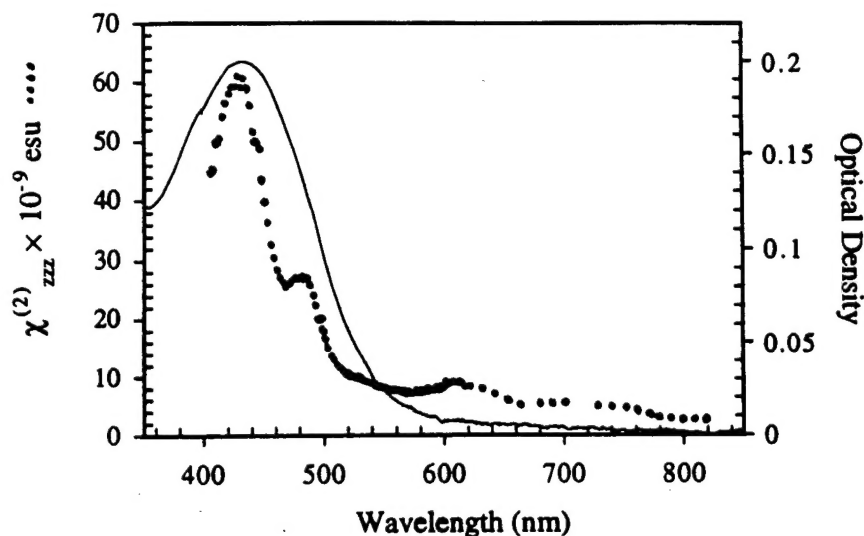


Figure 9. Linear optical absorption (filled line) and second harmonic response (dotted line) of a DANS/PMMA film poled in an in-plane geometry.

from 1200 nm input radiation, 700 nm from 1400 nm input, 800 nm from 1600 nm input, etc. Note also that the SHG response in the 400-500 nm region is much narrower than the linear absorption (filled line). This is not typical of the same chromophore poled under less drastic conditions. Clearly, the poling has created a new species with optical absorption and NLO-excitable features in the near IR. What are these species? Preliminary theoretical studies (see later Section II for more details) have focussed on π radical cation aggregates.^{11,12} These are the first quantum chemical calculations on *open shell second-order chromophores* (those with unpaired electrons). We find that face-to-face dimeric structures (Figure 10) such as $(\text{DANS})_2^+$ have spectral features and NLO response (both magnitude

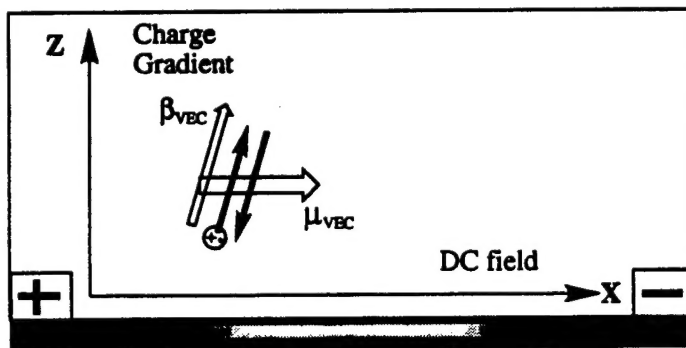


Figure 10. Model for the NLO response of a cation radical dimer in an in-plane poling geometry.

and polarization) characteristics in remarkable agreement with experiment.¹² To further verify that radical cation species are indeed being created, we were able to correlate the degree of charge injection with the concentration (by double integration spin counting techniques) of epr-active radical species detectable in samples of the poled films.¹¹ The epr spin Hamiltonian parameters are in good agreement with literature data for arylamine π radical cations (Figure 11).¹³ The significance of these results is many-fold:

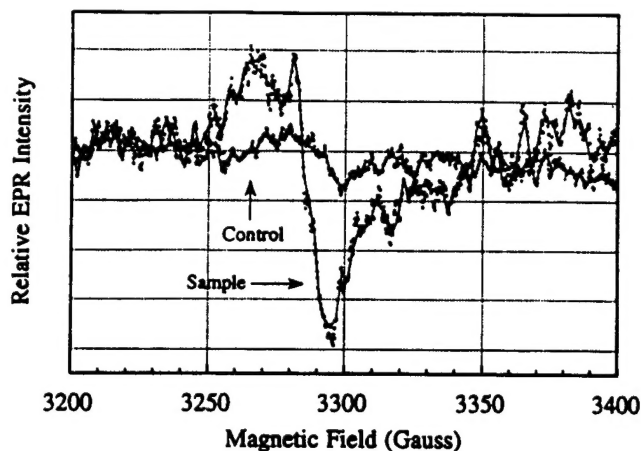


Figure 11. EPR spectrum of an in-plane poled DANS/PMMA film.

1. Optical losses in many poled films may be due to radical cation species caused by:
 - a. Poling
 - b. An oxidative atmosphere/light
 - c. Internal, thermally induced redox processes within the chromophore
2. It is conceivable that high β values measured by EFISH for some chromophores could also be due to π radical cations, and that optical features in the near IR are actually being brought into resonance.

It is imperative that more research be carried out in this area to understand poling/transparency degrading mechanisms and their generality.

D. Fluorinated Aryl Polyether-Based (FLARE) Polymers

Although polyimides certainly have many attractions both for microelectronic intermetal dielectric applications as well as for constructing NLO polymer systems, scientists at Allied-Signal Electronic Products have argued that FLARE (fluorinated aryl polyethers)¹⁴ have a number of unique attractions versus polyimides for dielectric applications. These include,

1. Lower dielectric constants (2.4-2.6 vs. 3.1-3.7)
2. Comparable or higher thermal/oxidative stability
3. Lower moisture absorption
4. Easier processability

These fluorinated polyethers can be readily synthesized from commercially available reagents (perfluorobiphenyl + a bisphenol), and in preliminary results¹⁵ we find that it is straightforward to introduce one of our chromophore modules (Figure 12). In the first experiments, we have obtained an

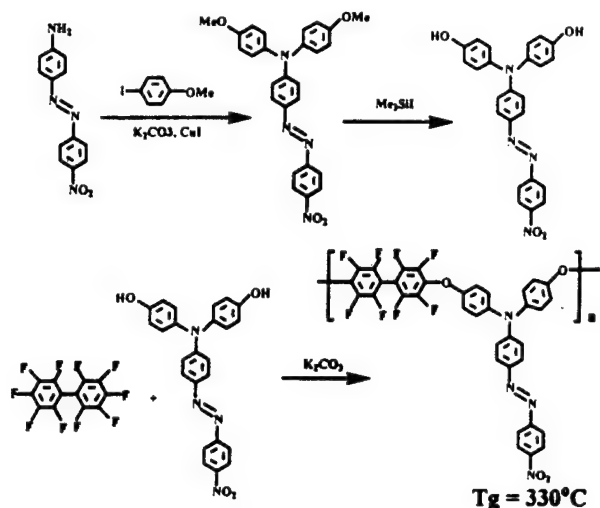


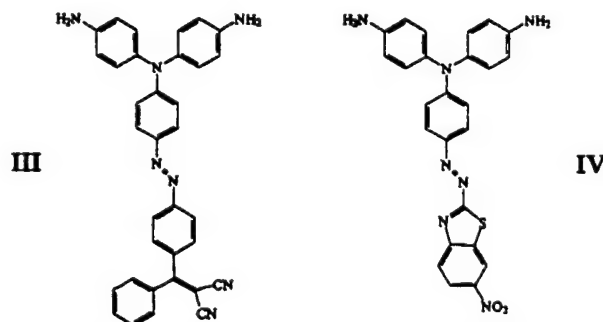
Figure 12. Synthetic approach to chromophoric FLARE polymers.

NLO-active polymer with $T_g = 330^\circ\text{C}$. Among the realistic possibilities for these types of materials are *reduced optical losses* arising from C-H and O-H stretching overtones in the near IR, lower susceptibility to oxidative degradation, lower moisture absorption, and lower dielectric constants. Clearly we want to continue work in the fluoropolymer area in the next contract period.

II. Chromophore Development. Experiment and Theory.

A. IBM-Northwestern Joint Study Agreement

One of the Northwestern NLO chemistry students, Mark Davey, spent most of the past year at IBM Almaden, working with Dr. R. Miller's group. The goal is to combine NU and IBM chromophore synthesis and chromophore incorporation expertises to produce unique, high- β , high thermal stability chromophores for incorporation into IBM and NU polyimide matrices. The synthetic effort will be followed by joint polymer processing and characterization efforts. The IBM staff has been delighted with Mark's progress, and several new and *highly efficient* approaches to chromophore modules have been developed. Some of the structures under study are shown below. Equally important, Mark has



had invaluable exposure to industrial research in a first-rate laboratory setting -- an ideal graduate student educational experience. Several joint manuscripts are in preparation.

B. The Theory of High- β Chromophores

As a closely integrated satellite to the poled polymer program, Mark Ratner and the PI's are continuing joint studies by SOS semiempirical formalisms of architecture-hyperpolarizability relationships in π electron chromophores.¹⁶ To increase the computational efficiency of this method, we have introduced the *correction vector* approach,¹⁷ which greatly reduces the CPU times required to analyze the structures and NLO responses of large, high- β chromophores. The goal is to understand chromophore characteristics relevant to improved devices and, ultimately, to design new "super chromophores" which should greatly enhance device performance.

We have analyzed in depth *environmental effects* on chromophore response as embodied in *solvation and counterion effects*.¹⁸ This analysis is important because in real-world devices, chromophores will be embedded in polymer matrices whereas most calculational schemes predict their properties in a vacuum. We have implemented an accurate and computationally efficient *self-consistent reaction field model* for calculating the effect of a dielectric medium on λ_{\max} and β_{vec} . The agreement with experiment is excellent (Figure 13). This technique has also been employed to evaluate the

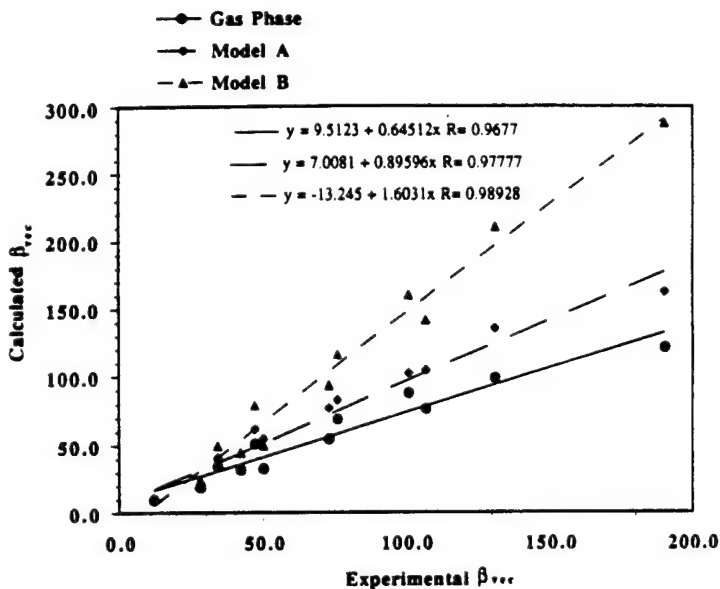


Figure 13. Comparison of calculated and experimental β_{vec} for a series of π -electron chromophores in the gas phase and in two types of polar solvation media.

validity of the bond length alternation (BLA) molecular response model (see below). Furthermore, we are employing these techniques to explore new ideas about generating large β values: whether molecules optically pumped to excited states could exhibit large β values (analogous to the large $\chi^{(3)}$ enhancement Heeger observed on pumping polyacetylene to an excited state). This work is still in progress, however initial studies,¹⁹ which required considerable code development, show that this idea is viable and should be pursued with additional theoretical studies.

Bond Length Alternation (BLA) concepts for understanding the linear optical properties of organic molecules are several decades old,²⁰ and have recently been insightfully applied to understanding molecular NLO response.²¹ Our interest has been to scrutinize theoretically at a very high level the basis of this model *in depth* and to explore the *generality* in regard to applicable

chromophore architectures and solvation/electric field effects. The result is a detailed, in-depth analysis that considerably expands what is known about BLA relationships for NLO applications.²² The conclusions for a diverse series of donor-bridge-acceptor-type chromophores are:

1. The field at which a chromophore geometry attains a cyanine-like structure *does not coincide with the field at which the first hyperpolarizability goes to zero*. A non-negligible asymmetry in the BLA pattern, associated with electronegativity differences between the terminal substituents, is required to attain the zero- β limit. At the zero- β limit, the polarizability exhibits a maximum and the second hyperpolarizability exhibits a very large negative value. The variation of all the three NLO coefficients is well accounted for by a limited number of low-lying states using two- and three-level models.
2. Applied electric fields produce large chromophore geometric variations and hence large variations in the linear and NLO properties. However, analysis of the solvent-dependent geometrical, linear, and NLO properties shows that in general *the static fields needed to produce these electronic and optical variations are unrealistically large*. Such variations are not produced by even the most polar solvents.
3. The molecular structure and optical property modifications are highly architecture specific; large solvent-dependent changes are observed only in chromophores which are stabilized substantially upon charge separation.
4. Chromophore NLO coefficients are found to match derivatives of the lower order NLO coefficients, as expected from formal definitions. However, the computed NLO coefficients and the NLO coefficients calculated by taking the derivative of the lower order NLO coefficient are *quantitatively different*.
5. In the chromophores studied, the optimum geometrical requirement for obtaining NLO response is when the conjugated bridge geometry lies between the polyenic and the cyanine-like structures. This is because the SHG coefficient is zero near the cyanine-limit while the THG coefficient exhibits a large negative value.

In summary, the use of an applied field to induce variations in chromophore molecular geometry and hence to study the changes in linear and NLO properties tends to overestimate the effects that would be, in reality, produced by a solvent.

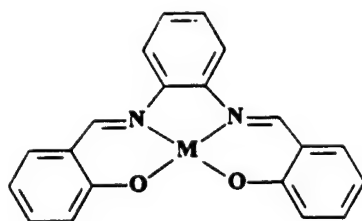
What is the appropriate strategy for optimizing β ? In a comprehensive study, the first phase of which has just been submitted for publication,²³ we show that β optimization should focus on the interplay between the *electron-excessivity* and *electron-deficiency* of the conjugated bridges connecting donor and acceptor substituents and on the aromaticity of the bridge. We find, for example, that *back-donation* from the bridges to the donor and acceptor substituents is a crucial factor in determining β . Although these structure- β effects are clearly evident in the experimental results of several groups, no one has fully explored the concepts from a theoretical standpoint. We show in a number of cases that $\mu\beta$ for several existing families of chromophores (good agreement between theory and experiment) can be substantially enhanced by simple changes in the electron excessivity and deficiency of the bridging architectures.

What should be done with this information? In a study in progress on two-dimensional chromophores, for example, we show that simple rearrangement of substituents on porphyrin skeletons²⁴ leads to dramatic enhancements in NLO response (e.g., $\mu\beta = 11,000$ at $h\nu = 0.1$ eV). Taking these concepts one step further, we have designed several chromophore structures with calculated

non-resonant $\mu\beta$ values of 100,000 - 200,000 at $h\nu = 0.1$ eV! At this point, we are considering how we might synthesize these structures and whether we should seek patent coverage!

C. Metal-Organic and Open Shell Chromophores

Although metal complexes are sometimes thought of as fragile, copper phthalocyanine can be sublimed unchanged at 500°C, can be recovered from concentrated H_2SO_4 unchanged, and is used in many types of outdoor paints. Clearly coordination complexes can be very robust. Since metal substituents also offer a means to tune NLO response and to bind chromophores to polymer matrices, we are involved in a collaborative computational theoretical, synthetic, and measurement chromophore development project with groups at U. of Catania, Italy (S. DiBella, I. Fragala) and CNET, France (I. Ledoux). Initial work has targeted simple Schiff's base structures such as those shown below. These simple, chemically robust complexes have non-resonant β_{vec} values as high as 2x DANS, T_d as high as



360°C, and exhibit substantial metal tuning of the NLO response.²⁵

As noted above, little theoretical (or experimental) work has been carried out on *open shell* chromophores. The motivations here are both to understand the linear optical and NLO response of conceivable chromophore oxidative, photolytic, or thermolytic products as well as to screen molecules with unusual electronic structures. The correct, chemically-oriented theoretical/computational

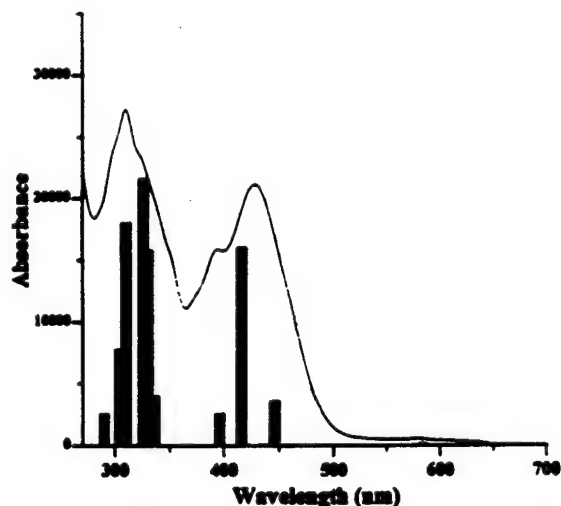


Figure 14. Comparison of experimental (filled line) and theoretical (bars) linear optical spectra for the complex Co(salophen).

formalism has been developed to attack such problems, and preliminary results show good agreement between calculated and experimental linear optical spectra (Figure 14).²⁶ Initial NLO calculations

reveal systems in which the open shell structure gives rise to new electronic states and significant responses (up to 3x DANS).

III. Intrinsically Acentric Self-Assembled Chromophoric Superlattices

Considering the great challenges inherent in fabricating, processing, electric field poling, and stabilizing electro-optic device structures based upon poled glassy polymers, it seems to us not inappropriate to investigate long-range, generalizable strategies which *do not require poling*. For several years, we have been investigating approaches to second-order NLO materials based upon molecular self-assembly.²⁷ Although early work revealed that acentric multilayers with large responses could indeed be synthesized, the fabrication process was tedious and the structural regularity modest. We have now achieved a *break-through* in the fabrication²⁸ which reduces the process to three simple steps (see below): i) coupling layer: dip and rinse, ii) chromophore layer: spin coat and flash evaporate (or deposit by CVD), iii) capping layer: dip and rinse.²⁸ This procedure allows assembly of one trilayer/-

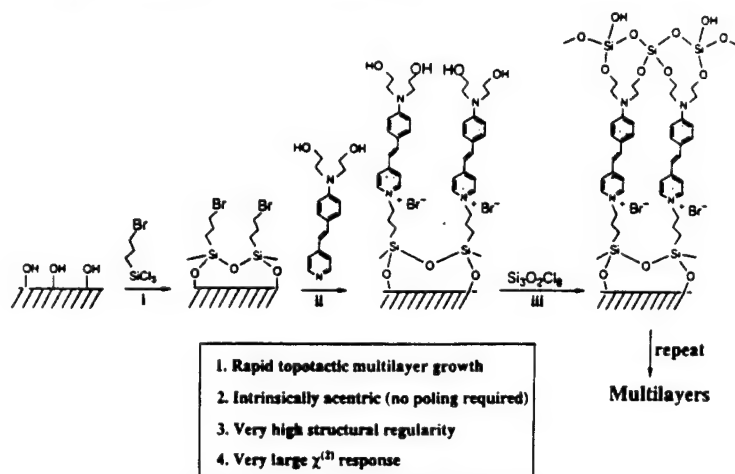


Figure 15. Procedure for the topotactic self-assembly of regular chromophoric superlattices.

60-90 minutes. By the highly linear scaling of λ_{\max} , $(I_{2\omega})^{1/2}$ (Figure 16), ellipsometric thickness, and x-ray reflectivity-derived thickness with the number of trilayers, it is evident that these films have *very high*

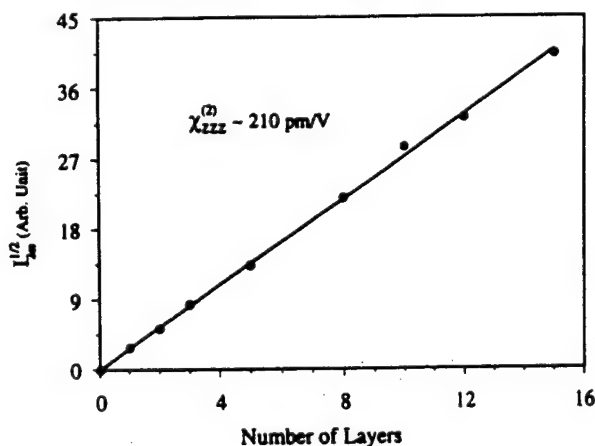


Figure 16. Plot of the square root of the second harmonic intensity versus the number of layers (each composed of steps i-iii in Figure 15) for the multilayer structure shown in Figure 15.

structural regularity. Using the OPA, $\chi_{33}^{(2)} \approx 210$ pm/V ($\lambda = 1064$ nm; slightly resonant) and ≈ 100 pm/V ($\lambda = 1400$ nm; off resonance).²⁹ The films are extremely smooth with, for example, an rms roughness of 12 Å by AFM for a 10 trilayer, 350 Å thick film, cannot be rubbed off, are impervious to most solvents, and exhibit stable NLO response at 80°C for extended periods. A simple evanescent hybrid waveguiding device (poly(methylmethacrylate) guiding layer, 200 Å active layer on float glass) emits bright blue light when pumped at 840 nm,³⁰ illustrating the microstructural uniformity and smoothness of these self-assembled films. In related work, we have studied the microstructures of these materials in some detail as a function of coupling layer and chromophore architectures.^{27,31} Beyond the immediate NLO applications, we feel that the knowledge base established by these studies will be applicable to the construction of numerous other optically functional structures where precise spatial positioning and locking into place of functional molecular building blocks is essential.

IV. New Instrumentation and Facilities

The dispersion of $\chi^{(2)}/r$ is invaluable information both for understanding the mechanism of molecular and bulk response as well as for obtaining engineering-level information useful for device design. Therefore, a "user-friendly" optical parametric amplifier, capable of simultaneously measuring 6 samples at a time, was constructed at Northwestern.²⁹ A large number of samples have been studied and the resulting dispersion data have provided valuable input to the theory effort. One of the Northwestern physics NLO students, Paul Lundquist, spent the final 6 months of his graduate career at Almaden as part of the IBM-Northwestern collaborative program (he is now a postdoctoral student at Almaden). Among the results of this interaction was the development of "user-friendly" instrumentation for expeditiously and accurately measuring thin film electro-optic coefficients in the *transmission geometry*.³² Such an approach allows simultaneous measurement of sample electro-optical, linear optical, and SHG properties. Moreover, sample alignment is more straightforward and there is less uncertainty in the derivation of r . We have performed these measurements on samples from several other AFOSR-supported laboratories. As part of the $\$110 \times 10^6$ remodeling of the Technological Institute at Northwestern, both the Marks and Wong groups moved into new laboratories. The synthesis, film processing, and NLO film characterization facilities are now first-rate.

REFERENCES

- For representative recent reviews of this subject, see:
 - (a) Lindsay, G.A.; Singer, K.D., Eds.; *Polymers for Second-Order Nonlinear Optics*, ACS Symposium Series 601; American Chemical Society, Washington DC, 1995.
 - (b) Dalton, L.R.; Harper, A.W.; Ghosn, R.; Steir, W.H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mutacich, R.V.; Jen, A.K.-Y.; Shea, K.J., *Chem. Mater.* **1995**, *7*, 1060.
 - (c) Marks, T.J.; Ratner, M.A., *Angew. Chem. Int. Ed. Eng.* **1995**, *7*, 426.
 - (d) Burland, D.M.; Miller, R.D.; Walsh, C.A., *Chem. Rev.* **1994**, *94*, 31.
 - (e) Zyss, J.; Ed., *Molecular Nonlinear Optics*, Academic Press, San Diego, CA, 1994.
 - (f) Marder, S.R.; Perry, J.W., *Adv. Mater.* **1993**, *11* 804.
 - (g) Zyss, J., Ed., *Molecular Nonlinear Optics Materials, Physics and Devices*. Academic Press, Boston, 1993.
- (a) Firestone, M.A.; Park, J.W.; Minami, N.; Marks, T.J.; Ratner, M.A.; Lin, W.; Wong, G.K. *Macromolecules*, **1995**, *28*, 2247.
 - (b) Firestone, M.A.; Marks, T.J.; Ratner, M.A.; Lin, W.; Wong, G.K. *Macromolecules*, **1995**, *28*, 2260.
 - (c) Firestone, M.A.; Ratner, M.A.; Marks, T.J. *Macromolecules*, **1995**, *28*, 6296.
- (a) Crumpler, E.T.; Reznichenko, J.L.; Li, D.; Marks, T.J.; Lin, W.; Lundquist, P.; Wong, G.K., *Chem. Mater.*, **1995**, *7*, 596-598.

- (b) Crumpler, E.T.; Marks, T.J., manuscript in preparation.
4. Crumpler, E.T.; Reznichenko, J.L.; Marks, T.J., unpublished observations.
 5. Geng, L.; Jen, A.; Marder, S.R.; Marks, T.J., unpublished results.
 6. (a) Geng, L.; Wang, J.-F.; Marks, T.J.; Lin, W.; Zhou, H.; Lundquist, P.M.; Wong, G.K. *Mater. Res. Soc. Sympos. Proc.*, **1996**, 392, 85-95.
 (b) Geng, L.; Wang, J.-F.; Marks, T.J.; Lin, W.; Lundquist, P.M.; Wong, G.K. *SPIE Proc.*, **1995**, 2528, 96.
 (c) Wang, J.-F.; Hubbard, M.A.; Jin, Y.; Lin, J.T.; Marks, T.J.; Lin, W.P.; Wong, G.K. *SPIE Proc.*, **1993**, 2025, 62.
 (d) Geng, L.; Wang, J.-F.; Marks, T.J.; Lin, W.; Wong, G.K., manuscripts in preparation.
 7. Zahir, S.; Chaudhari, M.A.; King, J. *Makromol. Chem., Macromol. Symp.*, **1989**, 25, 141, and references therein.
 8. Geng, L.; Lin, W.P.; Marks, T.J.; Wong, G.K., manuscript in preparation.
 9. (a) Teng, C.C.; Mortazavi, M.A.; Boudoughian, G.K., *Appl. Phys. Lett.* **1995**, 66, 667.
 (b) Kowalczyk, T.C.; Kosci, T.; Singer, K.D.; Cahill, P.A.; Seager, C.H.; Meinhardt, M.B.; Beuhler, A.J.; Wargowski, D.A., *J. Appl. Phys.* **1994**, 76, 2505.
 (c) Skumanich, A.; Jurich, M.; Swalen, J.D., *Appl. Phys. Lett.* **1993**, 62, 446.
 10. (a) Yitzchaik, S.; Berkovic, G.; Krongauz, V., *Chem. Mater.* **1990**, 2, 162.
 (b) Yitzchaik, S.; Berkovic, G.; Krongauz, V., *Macromolecules* **1990**, 23, 3539.
 (c) Yam, R.; Cohen, R.; Berkovic, G., *Nonlinear Opt.* **1995**, 11, 311.
 (d) Donval, A.; Berkovic, G.; Yilmaz, S.; Bauer-Gogonea, S.; Brinker, W.; Wirges, W.; Bauer, G.; Gerhard-Multhaupt, R. *Optics Comm.* **1996**, 123, 195.
 11. (a) Yitzchaik, S.; DiBella, S.; Lundquist, P.M.; Wong, G.K.; Marks, T.J.; Cohen, R.; Berkovic, G., *Phys. Rev. B*, in press
 (b) Yitzchaik, S.; Di Bella, S.; Lundquist, P.M.; Wong, G.K.; Marks, T.J., submitted for publication.
 (c) Di Bella, S.; Yitzchaik, S.; Fragala, I.; Marks, T.J.; Ratner, M.A., submitted for publication.
 12. (a) DiBella, S.; Lanza, G.; Fragala, I.; Yitzchaik, S.; Ratner, M.A.; Marks, T.J., manuscript in preparation.
 (b) DiBella, S.; Fragala, I.; Marks, T.J.; Ratner, M.A. *J. Am. Chem. Soc.*, in press.
 13. (a) Ayscough, P.B., *Electron Spin Resonance in Chemistry*, Methuen & Co.: London 1967, Chapter 8.
 (b) Melchior, M.T.; Maki, A.H., *J. Chem. Phys.* **1961**, 34, 471.
 (c) Rieger, P.H.; Fraenkel, G.K., *J. Chem. Phys.* **1963**, 39, 609.
 14. (a) Hendricks, N.H. *Solid State Technology*, **1995**, July, 117.
 (b) Mercer, F.W.; Sovish, R.C., U.S. Patent 5,115,082 (1992).
 15. Geng, L.; Marks, T.J., unpublished results.
 16. Kanis, D.R.; Ratner, M.A.; Marks, T.J. *Chem. Rev.* **1994**, 94, 195, and references therein.

17. Albert, I.D.L.; Marks, T.J.; Ratner, M.A. *ACS Sympos. Series* 1996, 628, 116-132.
18. (a) Albert, I.D.L.; DiBella, S.; Kanis, D.R.; Marks, T.J.; Ratner, M.A. *ACS Sympos. Series*, in press.
(b) DiBella, S.; Fragala, I.; Ratner, M.A.; Marks, T.J. *Chem. Mater.*, 1995, 7, 400.
(c) DiBella, S.; Marks, T.J.; Ratner, M.A. *J. Am. Chem. Soc.*, 1994, 116, 4440.
19. Albert, I.D.L.; Marks, T.J.; Ratner, M.A., unpublished results.
20. (a) Baeriswyl, D.; Campbell, D.K.; Mazumdar, S. In *Conjugated Conducting Polymers*, Keiss, H.G., Ed. Springer Series in Solid State Sciences, 102, Springer: Berlin 1992.
(b) Longuet-Higgins, H.C.; Salem, L. *Proc. Roy. Soc. London*, 1959, A251, 172.
21. (a) Marder, S.R.; Cheng, L.-T.; Tiemann, B.G.; Friedli, A.C.; Blanchard-Desce, M.; Perry, J.W.; Skindhoj, J. *Science*, 1994, 263, 511.
(b) Marder, S.R.; Perry, J.W.; Bourhill, G.; Gorman, C.B.; Tiemann, B.G. *Science*, 1993, 261, 183.
(c) Marder, S.R.; Gorman, C.B.; Perry, J.W.; Bourhill, G.; Bredas, J.-L.; *Science*, 1994, 265, 632.
(d) Meyers, F.; Marder, S.R.; Pierce, B.M.; Bredas, J.L. *J. Amer. Chem. Soc.*, 1994, 116, 10703.
22. Albert, I.D.L.; Marks, T.J.; Ratner, M.A.; *J. Phys. Chem.* 1996, 100, 9714.
23. Albert, I.D.L.; Marks, T.J.; Ratner, M.A., submitted for publication.
24. Albert, I.D.L.; Marks, T.J.; Ratner, M.A., manuscript in preparation.
25. (a) DiBella, S.; Fragala, I.; Ledoux, I.; Marks, T.J. *J. Am. Chem. Soc.* 1995, 117, 9481.
(b) DiBella, S.; Fragala, I.; Ledoux, I.; Diaz-Garcia, M.A.; Lacroix, P.G.; Marks, T.J. *Chem. Mater.* 1994, 6, 881-883.
26. DiBella, S.; Fragala, I.; Marks, T.J.; Ratner, M.A. *J. Am. Chem. Soc.*, in press.
27. Yitzchaik, S.; Marks, T.J. *Acc. Chem. Res.* 1996, 29, 197.
28. (a) Lin, W.; Lin, W.; Wong, G.K.; Marks, T.J. *J. Am. Chem. Soc.*, 1996, 118, 8034.
(b) Lin, W.; Yitzchaik, S.; Lin, W.; Malik, A.; Durbin, M.K.; Richter, A.G.; Wong, G.K.; Dutta, P.; Marks, T.J. *Angew. Chem. Int. Ed. Engl.* 1995, 34, 1497.
29. Lundquist, P.M.; Yitzchaik, S.; Zhang, T.; Kanis, D.R.; Ratner, M.A.; Marks, T.J.; Wong, G.K. *Appl. Phys. Lett.* 1994, 64, 2194.
30. (a) Yitzchaik, S.; Lundquist, P.M.; Lin, W.; Marks, T.J.; Wong, G.K. *SPIE Proc.* 1994, 2285, 282.
(b) Lundquist, P.M.; Lin, W.; Yitzchaik, S.; Marks, T.J.; Wong, G.K. submitted for publication.
31. (a) Roscoe, S.G.; Kakkar, A.K.; Marks, T.J.; Malik, A.; Durbin, M.K.; Lin, W.; Wong, G.K.; Dutta, P. *Langmuir*, in press.
(b) Roscoe, S.B.; Yitzchaik, S.; Kakkar, A.K.; Marks, T.J.; Xu, Z.; Zhang, T.; Lin, W.; Wong, G.K. *Langmuir*, in press.
(c) Lin, W.; Lee, T.-F.; Lyman, R.F.; Lee, J.; Bedzyk, M.J.; Marks, T.J., *J. Am. Chem. Soc.*, in press.
32. Lundquist, P.M.; Jurich, M.C.; Wang, J.-F.; Zhou, H.; Marks, T.J.; Wong, G.K., *Appl. Phys. Lett.*, 1996, 69, 901.

33. Verbiest, T.; Burland, D.M.; Jurich, M.C.; Lee, V.Y.; Miller, R.D.; Volksen, W. *Science*, 1995, 268, 1604.
34. (a) Takekoshi, T. *Adv. Polymer Sci.* 1990, 94, 2.
(b) Sillion, B. in *Comprehensive Polymer Science*, Allen, G.; Bevington, J.C., Eds., Pergamon Press: Oxford, 1989, Chapt. 30.
(c) White, J.E. *Ind. Eng. Chem. Prod. Res. Dev.*, 1986, 25, 395.
(d) Sroog, C.E. *J. Polymer Sci. Macromol.. Rev.* 1976, 11, 161.
35. Loss due to C-H overtones should be diminished by ~30-50% and from absorbed H₂O by substantially more. For a discussion of how such losses are estimated, see: Koike, Y.; Ishigure, T.; Nihei, E. *J. Lightwave Technol.*, 1995, 13, 1475.
36. We find this technique is *essential* for accurately resolving glass transition features in many crosslinked NLO polymer systems.
37. To be carried out at IBM Almaden.
38. (a) Wang, X.; Gillham, J.K., *J. Coatings Technol.*, 1992, 64, 37.
(b) Wisanrakkit, G.; Gillham, J.K. *J. Coatings Technol.*, 1990, 62, 35.
39. (a) Lohse, F. *Makromol. Chem., Macromol. Symp.*, 1987, 7, 1.
(b) Oleinik, E.F. *Adv. Polym. Sci.*, 1986, 80, 49.
(c) Dusek, K. *Adv. Polym. Sci.*, 1986, 78, 1.
(d) Rozenberg, B.A. *Adv. Polym. Sci.*, 1986, 75, 113.
40. (a) Frisch, K.C.; Klempner, D. in *Comprehensive Polymer Science*, Allen, G.; Bevington, J.C., Eds. Pergamon Press: Oxford 1989, Vol. 5, Chapt. 24.
(b) Backus, J.C., et al *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, 1988, Vol. 13, pp. 243-303.

Interactions/transitions

The Northwestern group currently has a "joint study agreement" in place with IBM Almaden, a similar agreement with ROITech, and a licensing agreement for polymer manufacture in place with Adtech. TJM visited both IBM and ROITech, and Som Soni of Adtech visited Northwestern. The result is that collaborative research projects have been launched with both IBM and ROITech. The former has taken the form of two Northwestern AFOSR NLO graduate students (one chemist, one physicist) spending time at Almaden. A great deal of valuable knowledge transfer has taken place in both directions, and several manuscripts are in preparation. Charles Lee had a chance to meet Paul Lundquist on a recent visit. Paul is very impressive and accepted a postdoctoral appointment at Almaden.

In regard to ROITech, we are presently attaching some of Alex Jen's chromophores to our polymers. Alex has also sent us samples for SHG and OPA measurements. At a later stage, we expect one of Alex's people to use our in situ poling apparatus to optimize their poling, curing, and processing techniques.

- a. The PI's and their students spoke on their NLO polymer research at ACS, APS, MRS, and SPIE national meetings.
- b. TJM is a contract consultant for Dow Chemical Co., Hoechst-Celanese, and Dow-Corning. He is on the Corporate Technical Advisory Boards of Dow and Dow-Corning. His role is to advise these corporations in the areas of catalysis, polymeric materials, electronic and electro-optic materials, and inorganic materials. He has served on several NSF, DOE, and ONR advisory panels.
- c. In the past year, TJM has spoken at ROITech, IBM, and AKZO.

New discoveries, inventions, patents

Patents:

- "Poled Polymeric Nonlinear Optical Materials" U.S. Patent 5,371,173 (1994)
- "Self-Assembled Superlattices and Waveguides Prepared for Use Therewith" U.S. Patent allowed (divisional in progress).

Disclosure:

- "Waveguide Cutoff Optical Switch"

Honors/ Awards (TJM)

- Series Advisory Editor, Oxford Monographs on the Physics and Chemistry of Materials
- Fellow, American Academy of Arts and Sciences
- Member, U.S. National Academy of Sciences
- USA Advisory Editor, Royal Society of Chemistry Chemical Communications
- Corporate Technical Advisory Board, Dow Corning Corporation, 1994-
- 1995 Lind Lecturer, University of Tennessee - Oak Ridge Nat. Lab.
- 1995 Fishel Lecturer, Vanderbilt University
- 1996 Musher Lecturer, Hebrew University of Jerusalem
- Corporate Technical Advisory Board, Dow Chemical Company, 1995-
- 1996 H.C. Brown Lecturer, Purdue University
- 1996 Xerox of Canada Distinguished Lecturer, (U. of British Columbia; Victoria U)
- 1997 Centenary Lecturer, Royal Society of Chemistry

1996 Kilpatrick Lecturer, Illinois Institute of Technology
 1996 Chairman-elect, ACS Division of Inorganic Chemistry
 1997 Chairman, ACS Division of Inorganic Chemistry
 1997 Siedle Lecturer, Indiana U.

Personnel Supported

Mark H. Davey (Graduate Student)
 Paul M. Lundquist (Graduate Student)

Publications

1. $\chi^{(2)}$ Dispersion and Waveguiding Measurements in Acentric Chromophoric Self-Assembled NLO Materials, S. Yitzchaik, P.M. Lundquist, W. Lin, T.J. Marks, and G.K. Wong, SPIE Proc., **2285**, 282 (1994).
2. Thermal Stabilization of Poled Polymeric NLO Materials Via Multifunctional Crosslinkers. The Effects of Epoxy and Diisocyanate Crosslinkers in Chromophore-Functionalized Poly(*p*-Hydroxystyrenes), E.T. Crumpler, D. Li, T.J. Marks, W. Lin, P.M. Lundquist, and G.K. Wong, Polym. Mater. Sci. Eng., **72**, 289 (1995).
3. Modular High-Tg Second-Order Polymeric Nonlinear Optical Materials. Polyfunctional Epoxide and Diisocyanate Crosslinked Chromophoric Polyhydroxystyrenes, by E.T. Crumpler, J.L. Reznichenko, D. Li, T.J. Marks, W. Lin, P.M. Lundquist, and G.K. Wong, Chem. Mater., **7**, 596 (1995).
4. Properties of Ultra-High-Tg Chromophoric Polyimides and Polyureas as High-Performance Nonlinear Optical Materials. Architecture-Processing-Temporal Stability Relationships, L. Geng, J.-F. Wang, T.J. Marks, W. Lin, P.M. Lundquist, and G.K. Wong, SPIE Proc., **2528**, 96 (1995).
5. Ultra-High-Tg Chromophoric Polyimides and Polyureas as High-Performance Nonlinear Optical Materials, L. Geng, J. Wang, T.J. Marks, W. Lin, H. Zhou, P.M. Lundquist, and G.K. Wong, Mats. Res. Soc. Sympos. Proc., **413**, 135 (1996).
6. Novel Spectral Characteristics of Second-Order Optical Nonlinearities in Poled Polymer Films Containing Charged Chromophore Aggregates, P.M. Lundquist, S. Yitzchaik, T.J. Marks, G.K. Wong, S. Di Bella, R. Cohen, and G. Berkovic, Phys. Rev. B, **55**, 14055 (1997).
7. Frequency Doubling In Novel Four-Component Self-Assembled Chromophoric Waveguide Structures, P.M. Lundquist, W. Lin, S. Yitzchaik, T.J. Marks, and G.K. Wong, Appl. Phys. Lett., **70**, 1941 (1997).
8. Electro-Optical Characterization of Poled Polymer Thin Films Using a Highly Accurate Transmission Technique, P.M. Lundquist, M.C. Jurich, J.-F. Wang, H. Zhou, T.J. Marks, and G.K. Wong, Appl. Phys. Lett., **69**, 901 (1996).
9. Anomalous Second-Order Nonlinear Optical Response of In-Plane Poled Glassy Polymers. Spectroscopic and Theoretical Support for the Importance of Charged Chromophore Aggregates, S. Yitzchaik, S. Di Bella, P.M. Lundquist, G.K. Wong, and T.J. Marks, J. Am. Chem. Soc., **119**, 2995 (1997).
10. A Novel Synthetic Approach For the Synthesis of Bis(4-aminophenyl)amino Substituted Chromophores For Use in Nonlinear Optics, M.H. Davey, V.Y. Lee, T.J. Marks, and R.D. Miller, Polymer Preprints, **38**, 261 (1997).